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Monolayers and Membranes from Amphiphilic Polymers

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Summary: Nanometer thin, elastomeric membranes with considerable application potential in micro mechanics and materials science can be prepared by transferring monomolecular layers of polymers with ionic head groups from the water surface to solid substrates with holes. If monolayers of liquid polymers are transferred to substrates with openings they initially cover the openings, but finally rupture within a couple of minutes after transfer. However, if the polymer monolayers are stabilised by vitrification, chemical or physical cross-linking, they can be transferred to cover openings in solids substrates as stable membranes. Especially if monolayers of low glass transition polymers are cross-linked, elastomeric membranes are obtained, which might find application in micro mechanical devices like membrane valves and pumps. Incorporation of either a second, incompatible polymer or hydrophobised colloids leads to laterally structured and porous membranes.

Introduction

The Langmuir-Blodgett (LB) technique offers the opportunity to generate suspended membranes by assembling a monolayer at the air-water interface and transferring it to cover a hole in a solid substrate. However, the preparation of suspended membranes via LB-transfer is generally more difficult than LB-transfer of thin organic coatings onto continuous smooth surfaces: Because it is not supported by an underlying substrate, the suspended membrane itself must be tough enough to withstand mechanical stress during fabrication and final use. Monolayers that are made from low molecular weight compounds or from liquid polymers easily rupture during transfer across a hole. Suspended membranes have been fabricated using glassy polymers, often stabilised by cross-linking [1 2]. These membranes are usually rigid. For certain applications, like membranes in micro mechanical valves and pumps, it might be advantageous to have elastomeric thin membranes available and to take advantage of the comparatively large reversible deformation of these materials.

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Membranes made from monolayers of anchored Polymers

When applied to a water surface, liquid polymers like perfluoropolyethers [3], polyisoprene [4], polybutadiene [5] or polydimethylsiloxane [6] with ionic head groups easily form smooth and continuous monolayers. By variation of the polymer chain length and surface concentration, the thickness of these monolayers can easily be tuned in the range of 10 to 100 nm thickness [7]. If these monolayers are transferred to substrates with openings (e.g. an electron microscopy grid) as schematically depicted in Fig. 1 they initially cover the openings as approximately 50 nm thin bilayers. However, these membranes rupture within minutes after transfer. As an example two snapshots of a membrane made via LB-transfer of polyisobutene with a single head group and a chain length of 300 repeat units is shown in Fig. 2. Within 30 minutes, all membrane-covered holes in the grid rupture.

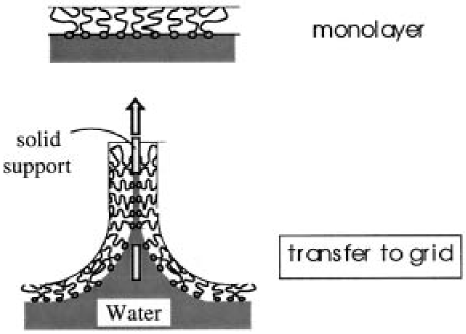

Fig. 1
Scheme of the formation of a freely suspended membrane via Langmuir-Blodgett transfer of an anchored polymer monolayer to substrates with openings.

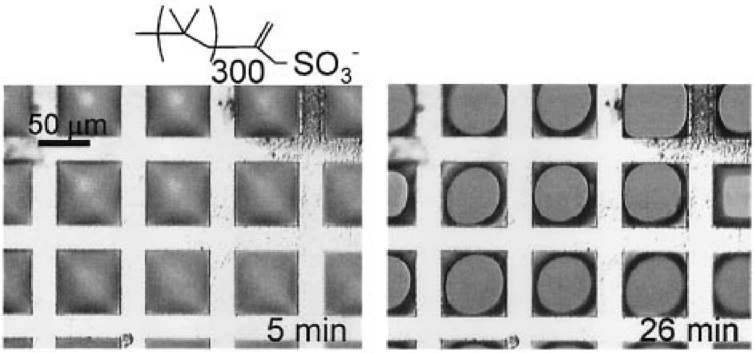

Fig. 2
A freely suspended membrane generated by Langmuir-Blodgett transfer of a monolayer of polyisobutene with a single ionic head group ruptures within 30 minutes. (Light microscopy image with top and bottom illumination.)

This rupture of the membrane can be expected; the membrane closely resembles a soapy membrane made out of a water core coated from both sides with a liquid layer of amphiphiles. Such membranes usually are metastable and rupture, especially if the water of the core region evaporates. However, the rupture can be suppressed and one can obtain stable membranes if the monolayer is solidified before or shortly after transfer. This solidification has been achieved here using three different principles: vitrification, photochemical chemically cross-linking and physical cross-linking.

Freely suspended membranes stabilised by vitrification have been prepared from monolayers of poly-4-*n*-butylstyrene with trimethylammoniumbromide head groups. Polybutylstyrene has a glass transition temperature of 25°C. Hence, at elevated temperatures polybutylstyrene with ionic head groups, applied to a water surface behave essentially like polyisoprenes at room temperature and form smooth and continuous monolayers. Upon cooling the polybutylstyrene monolayers vitrify to room temperature and thus can be transferred to yield solid freely suspended membranes.[8] (Fig. 3)

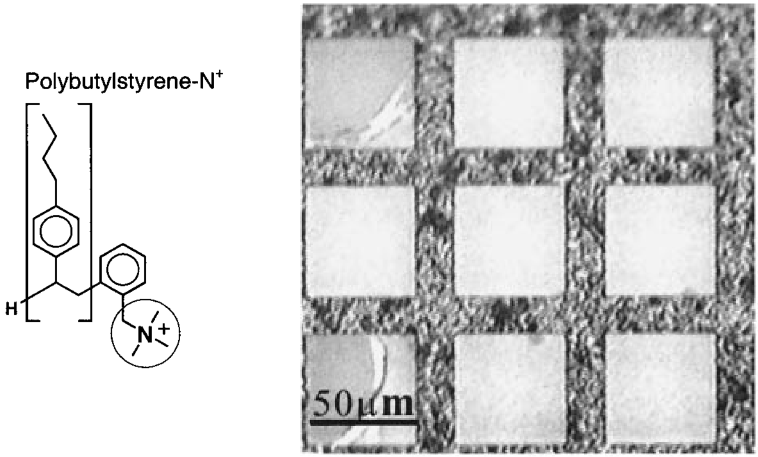

Fig. 3
Light microscopy image of an approximately 20 nm thick freely suspended membrane of polybutylstyrene-N$^+$ prepared by spreading at 40°C, cooling to 10°C and transfer to an electron microscopy grid.

Freely suspended membranes stabilised by chemical cross-linking have been obtained by irradiation of monolayers of polyisoprenes with ionic head groups and anthracene side chains. Upon irradiation with soft UV-light, the anthracene side chains dimerise (see Fig. 4 b). This dimerisation of side chains gives rise to permanent cross-linking points. Since the polyisoprene chains have a low glass transition temperature, this cross-linking transforms the initially liquid monolayer into a thin layer of an elastomer. This layer can easily be transferred across openings in solid substrates.[9] The resulting freely suspended membranes are long term stable (at least several months).

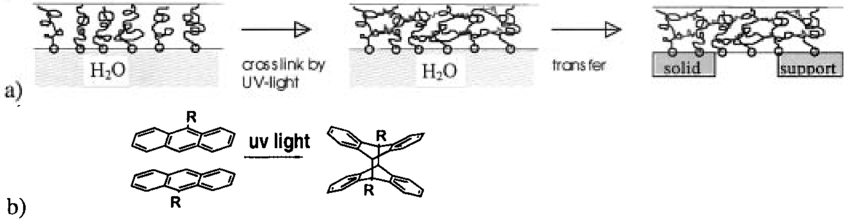

Fig. 4
Scheme of the preparation of elastomeric membranes via cross-linking of the side chains of anthracene tagged polyisopren with ionic head groups.

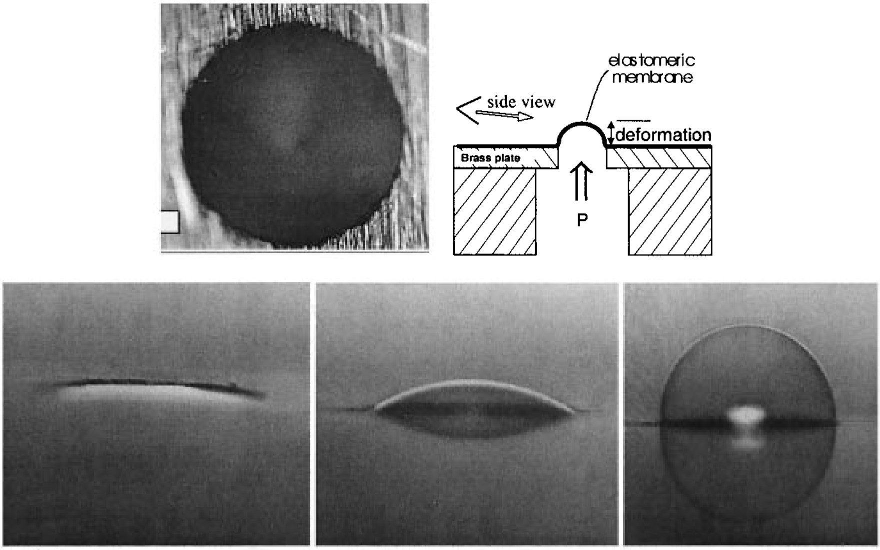

Fig. 5
Top and side view of an elastomeric cross-linked polyisoprene membrane reversibly deformed by a small overpressure from below.

The elastomeric properties of these freely suspended membranes can be shown by applying a small pressure from one side. When the pressure is applied, the membrane bulges. When the pressure is released, the membrane flattens itself reversibly. (see Fig. 5).

In this procedure the monolayer is cross-linked and converted into a solid layer on the water surface; after cross-linking it can sustain neither shear flow nor extensional flow. When a monolayer is transferred to a substrate, which is smaller than the Langmuir trough, it has to undergo two-dimensional flow, otherwise it will develop stress or will wrinkle, especially if several substrates are coated consecutively. Thus, in the experiments depicted above only small substrates were coated and most of the monolayer had to be discarded.

The two dimensional flow problem can be avoided by transferring liquid monolayers and cross-linking them shortly after the transfer. This can be accomplished quite easily by using polymers with more than one ionic group per chain. On the water surface, these polymers behave similar to the polymers with single ionic head groups. Like the linear polymers depicted in Fig. 2, the monolayers of the three arm star polymers can be transferred to cover holes in solid substrates. In the case of the star polymers, however, the ionic groups form inverted micelles when the membrane dries. These inverted micelles efficiently cross-link the polymer and thus give rise to the formation of elastomeric membranes without irradiation being necessary [10] (see Fig. 6).

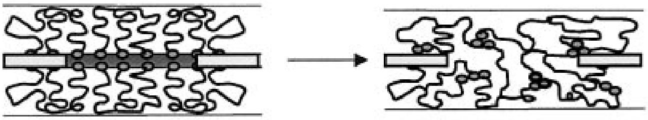

Fig. 6
Scheme of physical cross-linking of a suspended membrane of polymer chains with multiple head groups. Upon drying of the water core, which is initially present in the transferred membrane, the head groups aggregate and form physical cross linking sites.

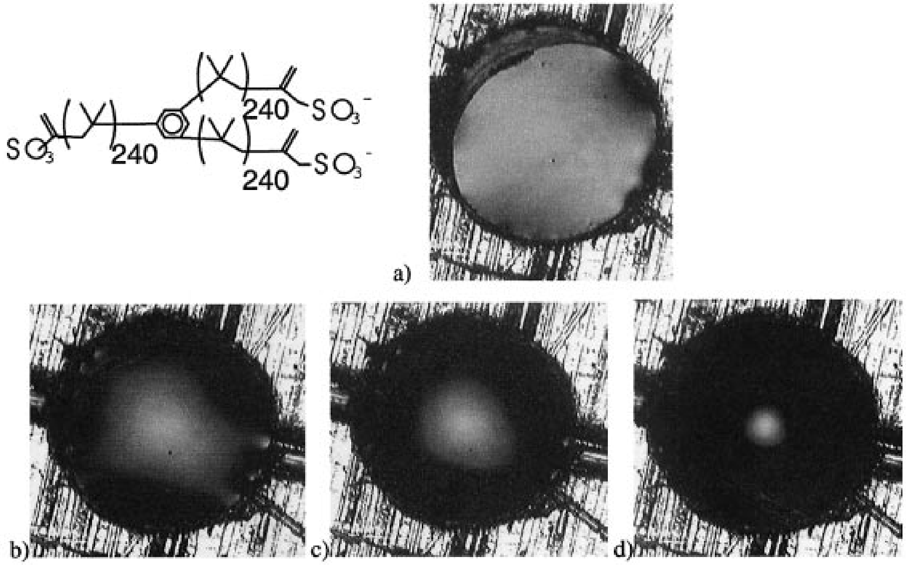

Fig. 7
Top view of an elastomeric polyisobutene membrane cross-linked via aggregation of multiple ionic head groups. a) Membrane spanning a 300 µm hole in a brass plate b) –d) Membrane bulges upward upon applying a small pressure from below.

Like in the case of photochemically cross-linked membranes, these physically cross-linked membranes are elastomeric. In Fig. 7 b) to d) a continuously increasing pressure of approximately 10-100 Pa is applied to a freely suspended membrane. The higher the applied pressure, the more does the membrane bulge upward. Upon release of the pressure this deformation is completely reversible and can be repeated multiple times.

Mixing the surface active polymers with a second component, e.g. an incompatible second polymer or hydrophobised colloidal particles gives rise to laterally structured monolayers and membranes. For example if anchored polybutylstyrene and anchored polyisobutylene with oppositely charged head groups are mixed and cospread on a water surface, one obtains monolayers with regular lateral pattern with micrometer periodicity.[11] The driving force for this pattern formation is the demixing of the two incompatible polymers, however, the detailed forces determining the morphology and controlling the size of the pattern are currently not completely understood.

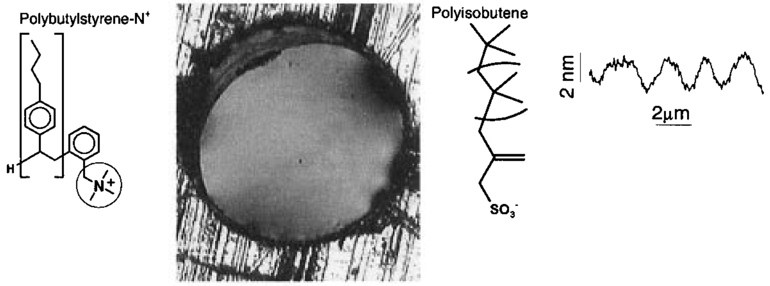

Fig. 8
Scanning force microscopy image and height profile of a mixed monolayer composed of polybutylstyrene with positively charged head groups and polyisobutene with negatively charged head groups.

Cospreading polymers with ionic anchor groups and hydrophobised silica colloids on a water surface, followed by transfer to solid substrates of electron microscopy grids gives rise to mixed monolayers. In these monolayers, domains of silica particles are embedded in a continuous matrix of a polymeric monolayers (see Figure 10 a).

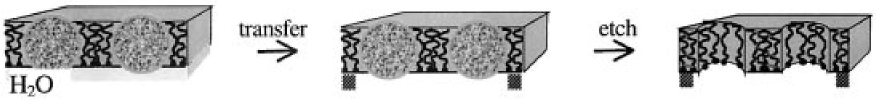

Fig. 9
Scheme of generating porous membranes via incorporation of colloids into polymeric monolayers, followed by cross-linking, transfer and removal of the colloids.

Exposure of these membranes to hydrofluoric acid vapour removes the silica particles. This gives rise to porous monolayers and porous membranes of controlled porosity with a uniform pore size distribution. These membranes are promising for applications like ultrafiltration, bio encapsulation and as masks and moulds for generating new nanoscopic and mesoscopic structures and surface patterns.

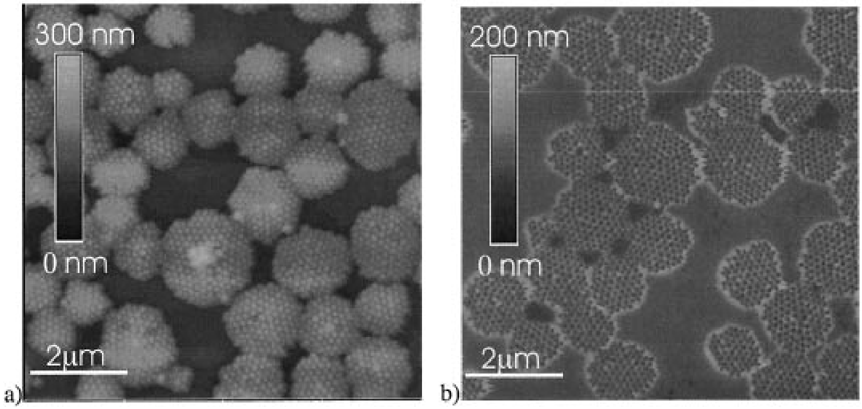

Fig. 10
a) hybrid monolayer composed of anchored polymers and silica colloids.
b) porous monolayer obtained after removal of the colloids.

Experimental

Linear polyisoprene with a sulfonate head group and anthracene side groups has been synthesised via living anionic polymerisation followed by platinum catalysed hydrosilylation of the sulfonate terminated parent polyisoprene as published in [4] and [9]; polybutylstyrene with ammonium head group has been synthesised via living anionic polymerisation as described in [8]; polyisobutenes with sulfonate head groups have been synthesised via living cationic polymerisation as described in [12-14]. Monolayers on a water surface were prepared using a 20 cm x 46 cm rectangular Langmuir trough made of polytetrafluoroethylene, equipped with one compression barrier and a floating barrier for the detection of the surface pressure via the Langmuir method (Lauda FW2, Germany). The polymers were usually spread from chloroform solutions which contained 0.05 weight percent of polymer and 10 weight percent of ethanol (polyisoprene, polybutylstyrene) or from 4×10^{-4} weight% solutions in Ethanol/Pentane mixtures (1/50 by weight) (polyisobutenes). UV-illumination was made through the thermostatted, transparent lid of the trough using an array of four 30 cm long fluorescence lamps mounted parallel in an (40×40) cm aluminium housing (Philips TL 36D 25/09N). The emission of the lamps was between 305 to 420 nm, maximum emission was at λ_{max} = 355 nm. 30 min before and during illumination, the air space above the air-water interface was flushed with nitrogen (5 l/min). Silica colloids coated with polyisobutene amphiphiles (mean radius = 70 nm, polydispersity = 11%, suspended in cyclohexane) were obtained from Utrecht Colloid Synthesis Facility, Van 't Hoff Laboratory for Physical and Colloid Chemistry, Utrecht University, The Netherlands.

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